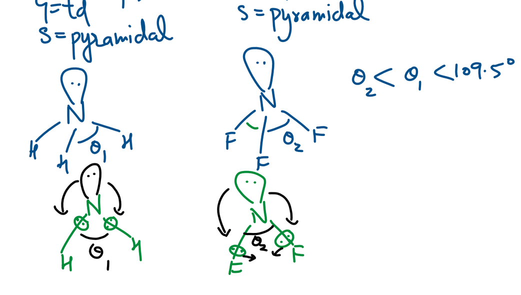

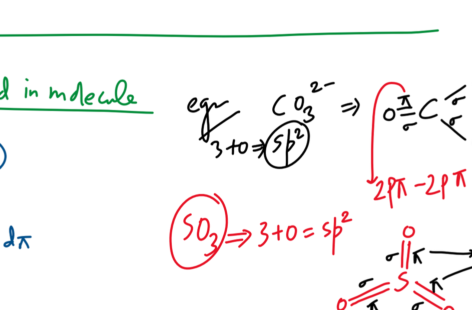

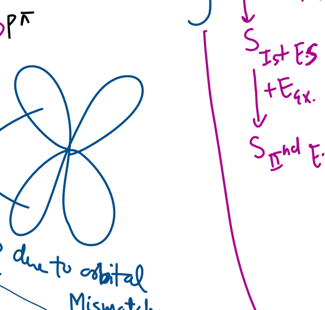

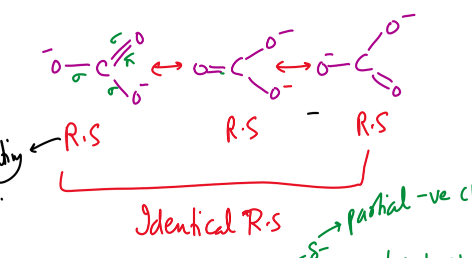

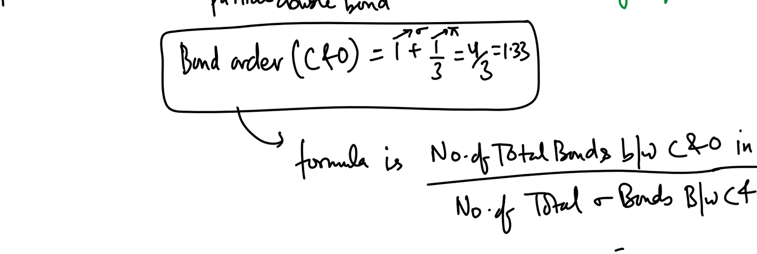

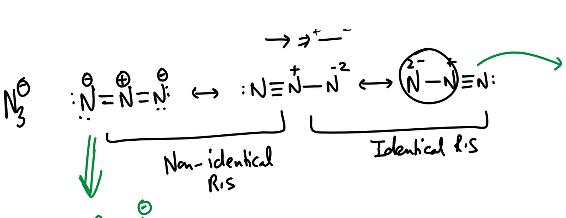

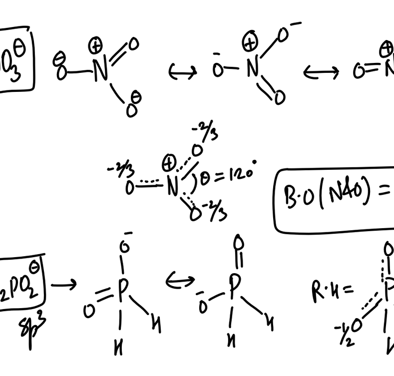

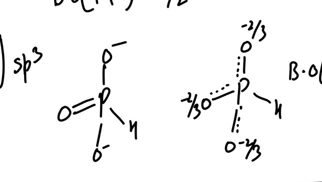

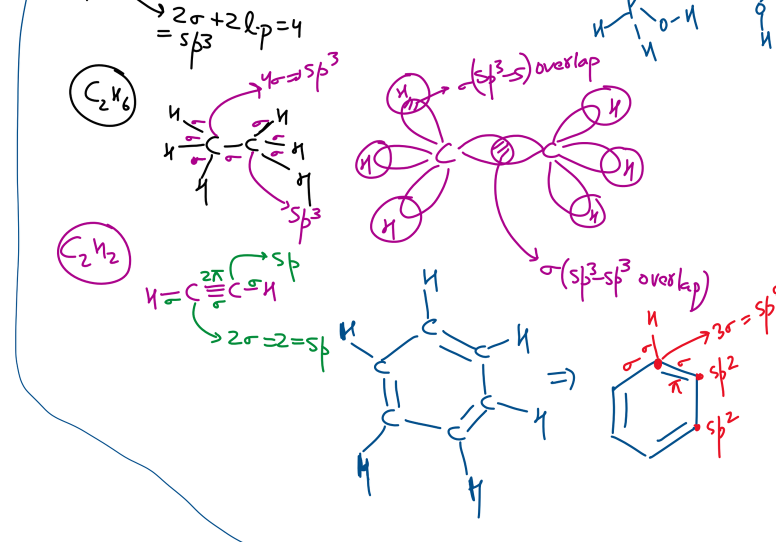

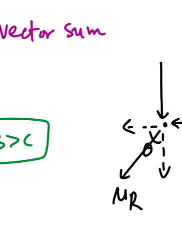

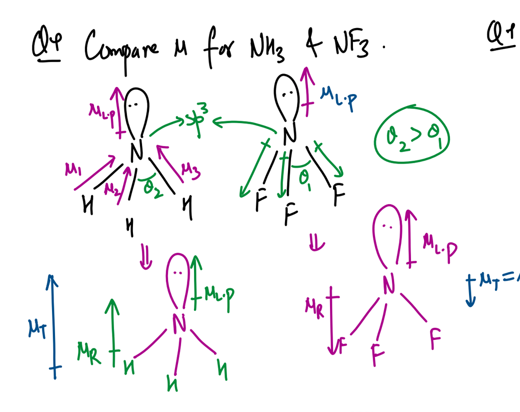

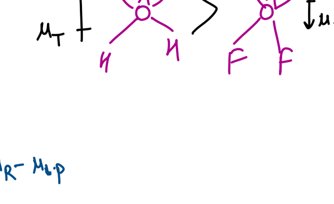

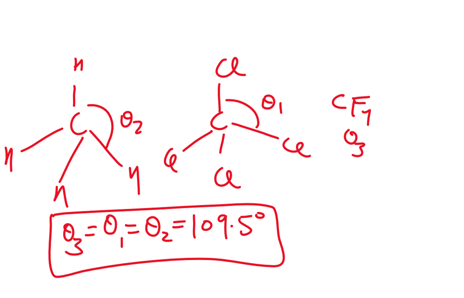

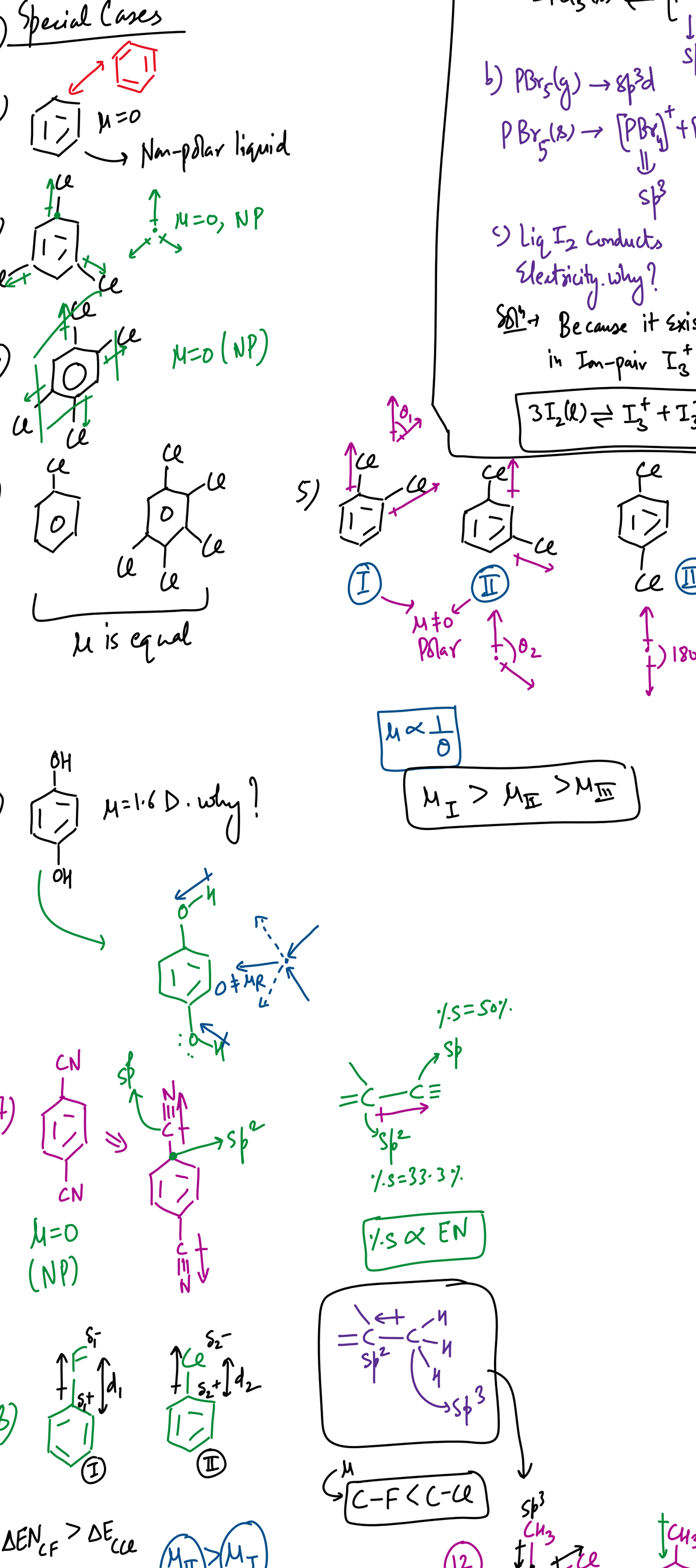

Bonding sep 29

Thursday, September 29, 2022 3:33 PM

⑤ Rule I for Bond Angle

Keeping Center Atom (Must have L.p) SAME; if EN of Surrounding atom ↑es, Bond Angle ↓es.

eg: i) NH_3 & NF_3

3+1=4 (sp^3) G=td S=pyramidal

3+1=4 (sp^3) G=td S=pyramidal

(ii) OF_2 < H_2O

103° 104.5°

N
H
H
H
θ₁
F
F
F
θ₂

$\theta_2 < \theta_1 < 109.5°$

Rule II

Keeping surrounding Atom same; if EN of center atom (must have L.p) ↑es; Bond Angle ↑es.

EN ⇒ N > P > As > Sb > Bi

eg: $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

107° 94° 93° 92° 91°

$H_2O > H_2S > H_2Se > H_2Te$

104.5° 92° 91° 90°

(H.W) Why there is a large difference b/w angles?

ⓗ Trick to find type of π Bond in molecule

sp ⟶ All π will be (pπ−pπ)

sp^2 ⟶ Ist π Bond ⇒ pπ−pπ & Rest π Bond ⟶ pπ−dπ

$\boxed{sp^3, sp^3d, sp^3d^2, sp^3d^3}$ ⟶ All π will be pπ−dπ

eg: CO_3^{2-} ⇒ 3+0 ⇒ sp^2

2pπ −2pπ overlap

(SO_3) ⇒ 3+0 = sp^2

→ 2pπ −3dπ or 3dπ −2pπ

→ 2pπ −3pπ

Explanation

$S = 1s^2 2s^2 2p^6 \boxed{3s^2 3p^4 3d^0}$

S ground =
3s 3p 3d
+E excitatⁿ
S Ist E.S =
+E ex.
S IInd E.S =
mix
sp² sp² sp² 3p 3d
σ σ σ
π π π
O O O

→ Aufbau Rule violated

$O = 2s^2 2p^4$

ⓗ XeO_2F_2

4+1 = 5 = sp^3d

2pπ −5dπ → weak overlap due to orbital Mismatch.

Note: Resonance :- Phenomenon in which e⁻ density delocalises (migrate, move) within the molecule or species & we are able to write more than 1 structure or LDS for molecule or species.

- ⊛ only e⁻ moves, not atom.
- ⊛ All Such Structures are Called Resonating structures (R.S) (or Canonical forms) & these are imaginary or Hypothetical representation.
- ⊛ Resultant of all these forms or R.S is called Resonance Hybrid (R.H).
- ⊛ R.H is real form & All the properties of Molecule/species are predicted from R.H → Like Bond length, Bond order, Bond Angle, Bond strength etc

eg: CO_3^{2-} ⟶ 3+0 = sp^2

⁻O
C
O
O⁻
O=C
O⁻
O⁻
O⁻
C
O
σ
π

Resonating str. ← R.S R.S R.S

Identical R.S

Bond str. SB < dB < TB

Bond length (S.B > d.B > T.B)

$H_2 \Rightarrow H-H$ B.O = 1

$O_2 \Rightarrow O=O$ Bond order = 2

$N_2 \Rightarrow N \equiv N$ Bond order = 3

R.H ⇒

-2/3
-2/3 = δ⁻ → partial -ve charge
-2/3
O
C
O
O
θ

$|\delta^-| = \left|\frac{2}{3} \times 1.6 \times 10^{-19} C\right|$

$|-2/3| < |-1|$

→ all C−O Bonds are of same length & same strength & they have angle of 120°.

partial double bond

$$\boxed{\text{Bond order } (C\text{–}O) = \overset{\sigma}{1} + \overset{\pi}{\frac{1}{3}} = \frac{4}{3} = 1.33}$$

formula is $\dfrac{\text{No. of Total Bonds b/w C\&O in any R.S}}{\text{No. of Total } \sigma \text{ Bonds B/w C\&O in any R.S}}$

eg SO_4^{2-}

θ_3
θ_1
θ_2
$\theta_1 = \theta_2 = \theta_3$

6 R·S

R·H ⇒

$-2/4 = -1/2 = \delta-$
$\theta = 109.5°$

$\text{Bond order}(S-O) = 1 + \frac{2}{4} = 3/2 = 1.5$

or

$6/4 = 3/2 = 1.5$

$N_3^{\ominus}$

→ ⇉ + — −
Non-identical R·S
Identical R·S

Bond length b/w N=N & N≡N

length

T·B < D·B < S·B

$NO_3^{\ominus}$

$-2/3$
$-2/3$
$-2/3$
$\theta = 120°$

$\boxed{B \cdot O(N-O) = 4/3}$

$H_2PO_2^{\ominus}$ → sp^3

$B \cdot O(P-O) = 3/2 = 1.5$

	(P-H) Bonds	(P-OH) Bonds	no. of H^+
H_3PO_4	0	3	3
H_3PO_3	1	2	2
H_3PO_2	2	1	1

HPO_3^{2-} sp^3

$B \cdot O(P-O) = \frac{4}{3}$

Structures of oxo-acids → oxygen containing acids

↳ To draw str, Remove all H^+ → Connected to oxygen and write str. for anion.

eg $H_2SO_4 \xrightarrow{-2H^+} SO_4^{2-}$

sp^3
sp^3
sp^3
σ
π

G = S = td

H.W

HNO_3 H_2SO_3
HNO_2 H_3PO_4

Except H_3PO_2 H_3PO_3

$2\sigma + 2l \cdot p = 4 = sp^3$

C_2H_6

$4\sigma ⇒ sp^3$
sp^3
$\sigma(sp^3-s)$ overlap
$\sigma(sp^3-sp^3$ overlap)

C_2H_2

2π
sp
σ
2σ = 2 = sp

⇒
3σ = sp^2
sp^2
sp^2
σ
π

Dipole Moment (μ) ⇒ for e^- shift in Covalent bond due to electronegativity difference. It is a vector quantity.

↳ represented by "⟼"

eg:- $H \rightarrow Cl$

$\delta+ \quad \delta-$
$H \rightarrow Cl$

Ionic character in covalent Bond

less EN atom

more EN atom

$\boxed{|\delta+| = |\delta-|}$ → less than charge of $1e^-$

q (Charge induced due to ΔEN)

$\mu_{HCl} = q \times \boxed{d}$ → Bond length of H-Cl

→ internuclear distance b/w H & Cl at max overlapping

(**) Bond b/w H & Cl is polar covalent Bond because $\boxed{\mu_{HCl} \neq 0}$

(**) $\mu_{H_2} = 0 \left[\begin{matrix} q = 0 \\ d \neq 0 \end{matrix}\right]$

H–H ↳ Non-polar covalent Bond

(*) L·p in s-orbital, p-orbital & d-orbital are not Considered for dipole moment.

(**) L·p in Hybrid orbital is considered for dipole moment Calculation.

↳ Hybrid orbital Lone pair Moment ($\mu_{L \cdot p}$)

Bond Moment :- e^- shift in any Bond when no. of Bonds > 1

Resultant Dipole moment is obtained by vector sum of all Bond Moments.

↓

μ_R

eg

μ_R
θ
μ_1
μ_2
A
B
C
θ

If $\boxed{EN:- A > B > C}$

μ_1 & μ_2 → Bond Moments

$$\mu_R = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\cos\theta}$$

for comparison,

θ↑, cos θ↓, μ_R↓ $\quad \boxed{\mu_R \propto \frac{1}{\theta}}$

μ_R
μ_R
μ_R
θ
θ
θ

Q4 Compare µ for NH_3 & NF_3.

$\mu_{l.p}$
μ_1
μ_2
μ_3
θ_2
sp^3
$\mu_{l.p}$
θ_1
$\theta_2 > \theta_1$
μ_T
μ_R
$\mu_{l.p}$
μ_R
$\mu_{l.p}$
N
H
F

$\mu_T = \mu_R - \mu_{l.p}$

$\mu_T (\mu_{Total}) = \mu_R + \mu_{l.p}$

$\boxed{\mu_{NH_3} > \mu_{NF_3}}$

μ_{NH_3} ⇓ 1.46 D; μ_{NF_3} ⇓ 0.25 D

(#) Also, μ_{NH_3} & μ_{NF_3} have non-zero value μ_T, so Both are polar molecules.

D → Debye → unit of Dipole Moment

$\boxed{1\,D = 3.3 \times 10^{-30}\ C \cdot m}$

Q1 Compare µ for H_2O & OF_2

μ_T
>
μ_T
H
H
F
F

(#) To predict where $\boxed{\mu_{Total} = 0}$ or $\mu_T \neq 0$ for species having single center atom.

$\mu_{Total} = 0$ ⇓ Non-polar molecules/species

$\mu_T \neq 0$ ⇓ polar molecules/species

ⓐ if L.p on center atom is zero and all surrounding atoms are same, then $\mu_T = 0$, Non-polar species

eg: PCl_5, BF_3, CH_4, CCl_4, $\boxed{CO_3^{2-}}$, SO_4^{2-}, PO_4^{3-}, NH_4^+, $[PCl_6]^-$, PCl_4^+ etc.

δ-
δ-
δ-
O
C
O
O
µ
µ
µ
120°
$\mu_R = 0$

$\mu = q \times d$

XeF_6 (P) µ≠0 6+1

SF_6 µ=0 (NP) 6+0

ⓑ if L.p on center ≠0, then μ_T may or may not be zero. Draw structure & guess yourself.

eg:- XeF_4 (4+2), SF_4

XeF_2 (NP) µ=0, $XeCl_2F_2$ (P) µ≠0, ClF_3 (P) µ≠0

F
Xe
F
F
F
S
F
F
F
F
I_3^+ ⇒
I
I
I
I_3^-
I
I
I

XeF_4: $\mu_T = 0$ (Non-polar) → Symmetric

SF_4: Non-symmetric, $\mu_T \neq 0$ (Polar)

I_3^+: $\mu_T \neq 0$ (Polar)

I_3^-: $\mu_T = 0$ (Non-polar)

H
C
H
H
H
θ_2
Cl
C
Cl
Cl
Cl
θ_1
CF_4
θ_3

$\boxed{\theta_3 = \theta_1 = \theta_2 = 109.5°}$

c) If L.p on center = 0 but all surrounding atoms are not same. μ_T may or may not be zero.

eg. PCl_3F_2, PF_3Cl_2 etc.

µ=0
(NP)
F
Cl
P
Cl
Cl
F
F
F
Cl
P
Cl
F
$\mu_T \neq 0$
(Polar)

Note: a) $PCl_5(g) \rightarrow sp^3d$

⇒ $PCl_5(s)$ exist as ion-pair form

$$2PCl_5(s) \rightleftharpoons \underset{sp^3}{[PCl_4]^+} + \underset{sp^3d^2}{[PCl_6]^-}$$

b) $PBr_5(g) \rightarrow sp^3d$

$$PBr_5(s) \rightarrow \underset{sp^3}{[PBr_4]^+} + Br^-$$

$[PF_6]^-$ ✓
$[PCl_6]^-$ ✓
$[PBr_6]^-$ ×
$[PI_6]^-$ ×

c) Liq I_2 conducts Electricity. why?

Sol → Because it exist in Ion-pair I_3^+ & I_3^-

$\boxed{3I_2(l) \rightleftharpoons I_3^+ + I_3^-}$

(#) Special Cases

1)

µ=0 → Non-polar liquid

2)

µ=0, NP

3)

µ=0 (NP)

4)

Cl
Cl
Cl
Cl
Cl
Cl

µ is equal

5)

Cl
Cl
Cl
Cl
Cl
Cl
θ_1
θ_2
180° = θ_3
I
II
III

I, II → µ≠0 Polar

III → NP, $\mu_{III} = 0$

$\boxed{\mu \propto \frac{1}{\theta}}$

$\boxed{\mu_I > \mu_{II} > \mu_{III}}$

6)

µ=1.6 D. why?

7)

CN
CN
sp
sp²
C≡N
C≡N

$\mu=0$
(NP)

% s = 50%
sp
sp²
% s = 33.3%

$\boxed{\% s \propto EN}$

% s = ⅓ × 100 = 33.3%
sp²
sp³
% s = 25%
sp²
sp
sp³
CH₃
sp²

$\boxed{\% s \propto EN}$

8)

δ₁−
F
δ₁+
d₁
I
δ₂−
Cl
δ₂+
d₂
II

$\Delta EN_{CF} > \Delta E_{CCl}$

$|\delta_1| > |\delta_2|$

$d_1 < d_2$

$\boxed{C-F < C-Cl}$

μ_{II}
μ_I
$|\delta_2|\times d_2$
$|\delta_1|\times d_1$

CH₃
Cl
(I)
CH₃
Cl
(II)
CH₃
Cl
(III)
θ = 0°

I < II < III

⑫

sp³
CH₃
Cl
μR
(I)
CH₃
Cl
(II)
CH₃
Cl
(III)
θ₃ = 0°
θ₂
μR

$\boxed{III > II > I}$

⑨ $HF > HCl > HBr > HI$

⑩ $CH_3Cl > CH_3F > CH_3Br > CH_3I$

H.W ⑪ $\underbrace{CH_3Cl > CH_2Cl_2 > CHCl_3}_{\mu\neq 0} > \underbrace{CCl_4}_{\mu=0}$

(#) Polarity in Covalent Bond is Ionic Character in covalent Bond.

$\overset{\delta+}{H}-\overset{\delta-}{Cl}$ → Ionic ch. (I.C)

→ Covalent ch. (C.C)

i) % Ionic Character in covalent Bond $= 16|\Delta EN| + 3.5|\Delta EN|^2$ → HANEY-SMITH Eqⁿ

ii) % Ionic character $= \left[1-e^{-\frac{1}{4}(\Delta EN)}\right]\times 100$

$\underset{2.1}{H}-\underset{4}{F}$ → $\Delta EN \approx 2$

$e = 2.72$

H–Cl

(iii) % I.C from use of Dipole moment

$\boxed{\% CC = 100 - \% IC}$

$$\% I.C = \frac{\mu_{observed}}{\mu_{calculated}} \text{ or } \frac{\mu_{experimental}}{\mu_{Theoretical}} \times 100$$

max dipole moment → By Assuming that Bond Breaks (Cleaves) 100%.

Q. Calculate % covalent character in A-B Bond having Bond length 1.62 Å and observed dipole moment is 0.4 D.

$\overset{\delta+}{A}-\overset{\delta-}{B}$

$A-B \xrightarrow[100\%]{} A^+ \; B^-$ (1.62 Å)

$q = 1.6\times10^{-19}\,C$

Sol:-

$$\% I.C = \frac{\mu_{obs}}{\mu_{cal}}\times 100$$

$$= \frac{0.4}{7.776}\times 100$$

$$= 5.144\%$$

$\mu_{cal} = q\times d$ → max Dipole moment

$$\mu_{cal} = 1.6\times10^{-19}\,C \times 1.62\times10^{-10}\,m$$

$$= \frac{1.6\times10^{-19}\times1.62\times10^{-10}\,Cm}{3.33\times10^{-30}\,Cm/D}$$

$$= 7.776\,D$$

$1\,D = 3.3\times10^{-30}\,Cm$

$$\% CC = 100 - 5.144\%$$

$$= 94.85\%$$